



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 664250		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEAA416)	
International application No. PCT/JP 03/15906	International filing date (day/month/year) 11.12.2003	Priority date (day/month/year) 11.12.2002	
International Patent Classification (IPC) or both national classification and IPC C30B25/02			
Applicant AMMONO SP. Z O.O.			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 9 sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the opinion</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input type="checkbox"/> Certain observations on the international application</p>			
Date of submission of the demand 09.07.2004		Date of completion of this report 23.02.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized Officer Cook, S Telephone No. +31 70 340-3372 	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/JP 03/15906

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17):*

Description, Pages

1-7, 9-12, 14-22, 24-26, 28-42 as originally filed
8, 13, 23, 27 received on 14.07.2004 with letter of 09.07.2004

Claims, Numbers

1-13 received on 21.12.2004 with letter of 21.12.2004

Drawings, Sheets

1/6-6/6 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/JP 03/15906

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	3-13
	No: Claims	1,2
Inventive step (IS)	Yes: Claims	3-13
	No: Claims	1,2
Industrial applicability (IA)	Yes: Claims	1-13
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following document:

D1: WO 97/13891 A (GRZEGORY IZABELLA ;KRUKOWSKI STANISDAW (PL); STEPNIEWSKI ROMAN (PL) 17 April 1997 (1997-04-17)

Novelty

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1 and 2 is not new in the sense of Article 33(2) PCT.

The reasons are the following:

Claims 1 and 2 are drafted as independent product claims. The product for which protection is sought in claim 1 has the following technical characteristics:

nitride substrate with both main faces substantially consisting of non N-polar face and N-polar face; dislocation density of 5×10^5 /cm² or less; thickness more than 100 microns; the layer of bulk mono-crystal nitride contains at least one element of alkali metals (no lower limit specified); a layer of nitride grown thereon.

The remaining subject matter of claim 1 concerns solely details of how the substrate is produced: slicing from different layers grown by various methods (VPE, MOCVD, MBE)

The subject matter of claim 2, with regard to the technical characteristics of the claimed product, is identical to that of claim 1. Only the features relating to the preparation method are different.

Because the processing features do not themselves confer distinguishing product features, the products of claims 1 and 2 are considered identical.

In examples 1 (see page 7, lines 11-15) and 2, D1 discloses a nitride (i.e. GaN) substrate with both faces substantially consisting of a non N-polar face (i.e. Ga-polar face) and an N-polar face with a dislocation density of less than 10^5 /cm² on which a layer of nitride is grown. Example 2 mentions that the substrate has a thickness of 0.5 mm. Concerning the presence alkali metal, there will invariably be alkali metal elements present, albeit at trace

atomic levels, since absolute purity can never be assured.

The products disclosed in D1 are considered no different to the product of claims 1 and 2.

None of the prior art documents cited in the international search report teaches all the process steps of independent claim 3. The subject matter of claim 3 and claims 4-13 (insofar as they can be considered to be dependent on claim 3) is thus found to be novel and meeting the requirements of Article 33(1) PCT in the sense of Article 33(2) PCT.

Inventive step

The application addresses the problem of growing nitride substrates with sufficiently low dislocation densities for subsequent epitaxy and optoelectronic device fabrication. The method proposed in claim 3 involves several steps, the first (a) being the preparation of a bulk mon-crystal nitride from super-critical ammonia containing solution in which alkali metals are present because of the type of mineralizer used. Because of this growth method, it would seem necessary to protect (b) the surface of the bulk substrate to avoid diffusion of alkali metals (see p.7, lines 5-11 of description). To obtain the desired substrate it is necessary to slice off a layer (c) from the protected bulk layer. This sequence of steps does not seem obvious from the prior art and the application appears to provide an alternative route to the ELOG technique and the one described in D1 (reacting gallium with nitrogen) to produce high quality substrates. For this reason the subject matter of claims 3 and claims 4-13 (insofar as they are dependent on claim 3) appears to meet the criteria of Article 33(1) PCT, because it involves an inventive step in the sense of Article 33(3) PCT.

Industrial applicability

The claimed subject matter is considered to be industrially applicable and thus fulfilling the requirements of Article 33(4) PCT.

Final remark

The application does not meet the requirements of Article 6 PCT. It is not clear whether claims 4 to 6 are dependent on claim 3. Use of the word "preferably" in the claims renders unclear the scope of the subject matter for which protection is sought.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/JP 03/15906

substrate having a dislocation density of $10^6/\text{cm}^2$ or less as well as the value of FWHM of the X-ray rocking curve from (0002) plane less than 80 arcsec, preferably $10^6/\text{cm}^2$ or less, more preferably $10^4/\text{cm}^2$ or less.

5 In the supercritical ammono process, we have discovered that A-axis growth is faster 4 times or more than that of C-axis growth and A-axis growth in the supercritical ammono method makes a dislocation density decreased too much in comparison with C-axis growth in the
10 same supercritical ammono method. Therefore, according to the new aspect of the invention, we can get a template type substrate as shown in Fig.9 wherein the layer A) is a hexagonal shaped substrate having a pair of C-plane surfaces with edge periphery of M-plane having a diameter
15 of 1 inch or more, which is prepared from a substrate made by A-axis direction growth of bulk mono-crystal nitride in a supercritical ammonium solution containing at least one element of alkali metals. It is suprised that the substrate has a dislocation density of $10^4/\text{cm}^2$ or less.

20 The substrate according to the present invention is characterized in that even if the gallium-containing nitride layer B) or C) and layers B1) and B2) or C1) and C2) contain at least one element of alkali metals, the content is less than that of the layer A) prepared by
25 crystallization of nitride in a supercritical ammonium

Fig.2 is a graph showing the change in time of the pressure in the autoclave where $T=\text{const}$ and illustrates the relation between the changes in the pressure and the processes of dissolution and crystallization in the case of this invention;

Fig.3 is a vertical sectional view of the autoclave and the set of furnaces used for carrying out this invention;

Fig.4 is a perspective view of the apparatus used for obtaining bulk mono-crystalline gallium nitride;

Fig.5 is a graph showing the relationship between the solubility of GaN in the supercritical ammonia which contains potassium amides (with Mineralizer: $\text{NH}_3=0.07$) and the pressure, where $T=400^\circ\text{C}$ and $T=500^\circ\text{C}$; finally,

Fig.6 is a graph showing the change in time of the temperature in the autoclave for the purposes of this Example.

Fig.7A and 7B are schematic sectional views of the first embodiment of the template type substrate according to the present invention.

Fig.8A, 8B and 8C are schematic sectional views of the second embodiment of the template type substrate according to the present invention.

Fig.9 is a schematic plane view showing a process of making A-axis direction growth seed.

- a) compounds $AmBn$, where A means H^+ and/or metal, preferably alkali, NH_4^+ , Si, S, P, whereas B means halogens, S, P, and n and m mean corresponding stoichiometric coefficients not lower than 1 and/or
- 5 b) groups of species such as:
- S_4N_4 , S_2N_2 , SN, S_4N_2 , $S_{11}N_2$, P_3N_5 , P_4N_6 , PN,
 - PN_2^- , PN_3^{4-} , PN_4^{7-} , PN^- , PN^{2-} ,
 - $PNCl_2$, $P(NH)_2NH_2$, P_4S_{10} , $NP(SNH_4)_2$, $NPSNH_4SH$, $NP(SH)_2$, PNS,
- Sulfur or silicon species built in the crystalline lattice
- 10 of the gallium-containing nitride serve as donors; magnesium, zinc or cadmium are acceptors; dopants such as manganese or chromium in the crystalline gallium nitride lattice provide it with magnetic properties; whereas
- phosphor atoms are isoelectronic with respect to nitrogen
- 15 atoms, and thus they make the energy gap narrower than that in the pure gallium-containing nitride. Those species do not only cause the weakening of ammono-basic nature of the supercritical solvent, but they also modify optical, electrical and magnetic properties of the gallium-
- 20 containing nitride.

Dissolution of the gallium-containing feedstock is a reversible or irreversible process of formation, through the feedstock, of gallium compounds soluble in the supercritical solvent, for example gallium complexes.

higher temperature in the crystallization zone than in the dissolution zone. According to the invention, the chemical transport is preferably caused by convection.

Seed as it has already been mentioned, is crucial for obtaining desired bulk gallium- or aluminum-containing nitride mono-crystals in a process according to the present invention. In view of the fact that the quality of the seed is crucial for the crystalline quality of the bulk gallium- or aluminum-containing nitride mono-crystals obtained by the process according to the present invention, the seed selected for the process should have possibly high quality. Various structures or wafers having a modified surface can also be used. For example a structure having a number of surfaces spaced adequately far from each other, arranged on a primary substrate and susceptible to the lateral overgrowth of crystalline nitrides may be used as a seed. Moreover, a seed having a homoepitaxial surface, exhibiting n-type electrical conductivity, for example doped with Si, may be used. Such seeds can be produced using processes for gallium-containing nitride crystal growth from gaseous phase, such as HVPE or MOCVD, or else MBE. Doping with Si during the growth process at the level of 10^{16} to $10^{21}/\text{cm}^3$ ensures n-type electric conductivity. Moreover, a composite seed may be used and in such seed directly on a primary substrate or on a buffer layer made for example of AlN - a

27. 12. 2004

CLAIMS

JC17 Rec'd PCT/PTO 10 JUN 2005
10/538407
(76)

~~1. A substrate used for opto-electric or electrical~~

devices which comprises a layer of nitride grown by means of vapor phase epitaxy growth wherein both main surfaces of the nitride substrate are substantially consisting of non N-polar face and N-polar face respectively and the dislocation density of the substrate is $5 \times 10^5/\text{cm}^2$ or less, wherein the substrate has a thickness of 100 μm or more preferably 150 μm or more which is sliced from a portion of

the layer B1 and/or B2) in the combination layers of A) the layer of bulk mono-crystal nitride containing at least one element of alkali metals (Group I, IUPAC 1989), B1) the layer of nitride grown by means of MOCVD or MBE and/or B2) the layer of gallium-containing nitride grown by means of HVPE.

2. A substrate used for opto-electric or electrical devices which comprises a layer of nitride grown by means of vapor phase epitaxy growth wherein both main surfaces of the nitride substrate are substantially consisting of non N-polar face and N-polar face respectively and the dislocation density of the substrate is $5 \times 10^5/\text{cm}^2$ or less, wherein the substrate has a thickness of 100 μm or more, preferably 150 μm or more which is sliced from a portion of the layer C1) and/or C2) in the combination layers of A1)

the layer of bulk mono-crystal nitride containing at least

one element of alkali metals (Group I, IUPAC 1989), B) the
~~layer of nitride grown by vapor phase epitaxy growth, A2)~~

the layer of bulk mono-crystal nitride containing at least
one element of alkali metals (Group I, IUPAC 1989), C1) the
5 layer grown by means of MOCVD or MBE and/or C2) the layer
of gallium-containing nitride grown by means of HVPE.

3. A process of preparing a substrate for opto-electric
or electrical devices which comprises steps of:

(a) preparing a layer A) of bulk mono-crystal nitride
10 containing at least one element of alkali metals (Group I,
IUPAC 1989) to have a thickness for substrate by
crystallization of gallium or aluminum-containing nitride
on a seed from a super-critical ammonia-containing
solution; (b) forming a layer B) or C) of nitride by means
15 of vapor phase epitaxy growth on Al or Ga-polar face of the
layer A);

and (c) slicing the layer B) or C) off from the substrate
A) to get a substrate having a thickness of 100 μm or more
and a main surface substantially consisting of Al or Ga-
20 polar face.

4. A process of preparing a substrate for opto-electric
or electrical devices, wherein the step (b) comprises (b1)
forming a layer B1) or C1) of nitride by means of vapor
phase epitaxy growth on Al or Ga-polar face of the layer A)
25 and (b2) forming a layer B2) or C2) of nitride by means of

vapor phase epitaxy growth on the layer B1) or C1);

~~and (c) slicing the layer B2) or C2) off from the substrate~~

A) to get a substrate having a thickness of 100 μm or more
and a main surface substantially consisting of Al or Ga-
5 polar face.

5. A process of preparing a substrate for opto-electric
or electrical devices, which further comprises (d) forming
a layer D) of nitride by means of vapor phase epitaxy
growth on Al or Ga-polar face of the layer B), C), B2) or
10 C2).

6. A process of preparing a substrate for opto-electric
or electrical devices, which further comprises (d) forming
a layer D) of nitride by means of vapor phase epitaxy
growth on Al or Ga-polar face of the layer B), C), B2) or
15 C2);

and (e) slicing the layer D) off from the substrate B), C),
B2) or C2) to get a substrate having a thickness of 100 μm
or more and a main surface substantially consisting of Al
or Ga-polar face.

20 7. A process of preparing a substrate for opto-electric
or electrical devices, according to any one of claims 3 to
6, wherein the layer B), B1), C) or C1) is prepared by
MOCVD and has a thickness of 0.1 to 3 μm .

8. A process of preparing a substrate for opto-electric
25 or electrical devices according to claim 7, which comprises

further step of polishing one of the faces of the layer B),
~~B2), C) or C2) to get a substrate for vapor phase epitaxy.~~

9. A process of preparing a substrate for opto-electric or electrical devices according to any one of claims 3 to 8, which comprises further step of annealing the substrate B),
5 B2), C) or C2). in the atmosphere that does not contain hydrogen at temperature between approx. 600 and 1050°C, thus producing material with better crystalline quality than before the annealing.

10. A process of preparing a substrate for opto-electric or electrical devices according to any one of claim 9, wherein the step of annealing is carried out in the atmosphere of inert gas with an addition of oxygen between
10 and 30 vol.%. .

11. A process of preparing a substrate for opto-electric or electrical devices according to claim 9, wherein the the step of annealing is carried out in a single step or in multiple steps until the desired level of impurities (such as hydrogen and/or ammonia or ions formed from the
15 impurities formed during the crystallization and/or annealing process) is reached.

12. A process of preparing a substrate for opto-electric or electrical devices according to any one of claims 3 to 11, which comprises further step of removing impurities
20 from bulk mono-crystalline nitride by a process of rinsing

in the environment of supercritical ammonia-containing

~~solvent, water or carbon dioxide or being subjected to the~~

action of gaseous hydrogen, nitrogen or ammonia.

13. A process of preparing a substrate for opto-electric
5 or electrical devices according to claim 12, wherein the
step of rinsing is carried out with aid of the application
of ultrasounds or the exposure to an electron beam.